

THE FEATURES OF SELF-ASSEMBLING ORGANIC BILAYERS
IMPORTANT TO THE FORMATION OF ANISOTROPIC INORGANIC MATERIALS
IN MICROGRAVITY CONDITIONS

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Hypothesis and objective.

There is a growing need for inorganic anisotropic particles in a variety of materials science applications. Structural, optical, and electrical properties can be greatly augmented by the fabrication of composite materials with anisotropic microstructures or with anisotropic particles uniformly dispersed in an isotropic matrix. Examples include structural composites, magnetic and optical recording media, photographic film, certain metal and ceramic alloys, and display technologies including flat panel displays. While considerable progress has been made toward developing an understanding of the synthesis of powders composed of monodispersed, spherical particles, these efforts have not been transferred to the synthesis of anisotropic nanoparticles.¹⁻³ The major objective of the program is to develop a fundamental understanding of the growth of anisotropic particles at organic templates, with emphasis on the chemical and structural aspects of layered organic assemblies that contribute to the formation of anisotropic inorganic particles.

There are two ways that anisotropically shaped particles have been produced from solution.⁴ The first is crystallographically controlled growth, producing particle shapes dictated by the relative growth rate among the various habit planes. Growth rates are often controlled by the inclusion of adsorbates or "poisons" that selectively restrict the growth of certain faces. A second approach is to control nucleation and growth by the synthesis of materials in the presence of molecular templates. While this method has been successfully used to restrict the size of particles,^{5,8} there have been few attempts to control particle shape. The current project applies principles from both of these approaches to achieve particle shape control by employing amphiphilic molecules assembled into specific lyotropic micellar structures as templates for the formation of anisotropic inorganic particles. An important aspect of our approach is to include careful analysis of the chemical nature of the particle/template interface, as this interaction can play an equally important role in determining the shape and orientation. As part of our studies, we make extensive use of model membrane systems prepared by Langmuir-Blodgett (LB)⁹ methods in order to efficiently survey possible template systems and establish the important chemical and

geometric features of the templates that influence particle growth. Our hypothesis is that uniform dispersions of anisotropic inorganic particles can be produced with templating methods if the chemical interaction between the organic template and the particle is carefully controlled.

Our initial work has now lead to LB model studies of silver and gold particles at organic templates. Silver particles are grown from silver nitrate solutions at monolayer templates formed from negatively charged surfactants. Gold particles have been formed photochemically by decomposing AuCl_4^- at positively charged monolayers.¹⁰ Plate-like platinum and silver particles have now been fabricated at lyotropic micellar templates,¹¹⁻¹³ and free standing bilayer templates have also been used to prepare other inorganic particles.^{14,15}

Justification for Microgravity Experiments.

The advantages of a microgravity environment for studying crystallization, nucleation and growth processes are well documented.^{16,17} In the present project, minimizing convectional induced fluid shear and sedimentation in the microgravity environment should allow extended structure organic templates to form rather than fragments or "rafts" that result at normal Earth's gravity. Convection limits the size of uniform template domains and also creates a non-uniform size dispersion. These imperfections in the template structures make it difficult to assess the role that the chemical and geometric identities of the template play in controlling particle size and dispersion. Reducing convection will also minimize the agglomeration of particles that are produced. Sedimentation is less of a problem than convection in the synthesis and processing of nanoscale particles or particles with nanometer scale in at least one dimension. Analysis¹⁸ demonstrates that the displacement due to gravity becomes less dominant as the particle size becomes smaller than about 0.25 μm . In contrast, sedimentation will begin to mask template effects as particle sizes increase beyond several hundred nanometers.

Langmuir-Blodgett Template Model Studies.

Four organic surfactants with different headgroups (PO_3^{2-} , OSO_3^- , SH , COO^-) have been spread onto an aqueous silver nitrate solution. The resulting Langmuir films were then transferred onto different hydrophobic substrates to form multilayered LB films. Exposure of these films to formaldehyde vapor results in the formation of quasi-spherical silver particles that range in size from 10 to 20 nm within one day. Further exposure to formaldehyde vapor leads to coalescence of these nanoparticles to give three-dimensional aggregates that have been characterized by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM).

The electrochemical formation of two-dimensional silver films under monolayers of the same four organic surfactants has also been studied. The reduction of silver cations to give metallic silver is achieved by applying a constant potential (from -0.2 V to -2V vs an SCE electrode used as the reference electrode) between a working electrode that just touches the surface of the aqueous subphase and a counter-electrode immersed into it. Within 1 to 10 minutes (depending on the nature of the surfactant which is used), a shiny, mirror-like, silver film can be observed at the organic monolayer-subphase interface. Optical microscopy and TEM have allowed us to determine the fractal structure of these films, which are constituted by interconnected and

randomly oriented 50-100 nm silver particles. The nature of the organic surfactant, but also the organization of the Langmuir monolayer has a strong effect on the electrocrystallization process.

Gold nanoparticles¹⁰ were generated by ultraviolet irradiation of Langmuir-Blodgett (LB) films of octadecylamine (ODA), 4-hexadecylaniline (HDA) and benzyldimethylstearylammmonium chloride monohydrate (BDSAC) deposited from aqueous HAuCl_4 subphases. In contrast, no gold crystals were observed in irradiated LB films prepared from monolayers of dipalmitoyl-DL- α -phosphatidyl-L-serine (DPPS) and dipalmitoyl-L- α -phosphatidylcholine (DPPC). The optical properties of colloidal gold provide an opportunity to monitor the formation of gold particles with UV-visible spectroscopy. Figure 1 shows the time evolution of the absorption spectra of a 13 layer ODA LB film under UV illumination over 30 min. It can be seen that the absorption band at 330 nm, which is assigned to the AuCl_4^- species, initially decreases and a strong plasmon band around 550 nm appears with increased irradiation time. At the same time, the LB film changes gradually from colorless to deep purple, indicating that the photoreduction of gold ions to zerovalent gold nanoparticles occurs very efficiently.

The absorption spectra of 11 layer films of BDSAC and HDA LB also show the gradual appearance of a plasmon band around 550 nm upon irradiation, indicating that metallic gold particles are formed and grow under UV irradiation. However, these absorption peaks are less intense than the band shown in Figure 1 for the ODA film. The reduced intensity is also obvious to the naked eye as the final purple color of the BDSAC and HDA LB films is much less pronounced than that of the ODA LB film. No change in the color of a white 10 layer DPPS LB film was observed after up to two hours of UV illumination, and there was no change in its UV-visible spectrum over that time.

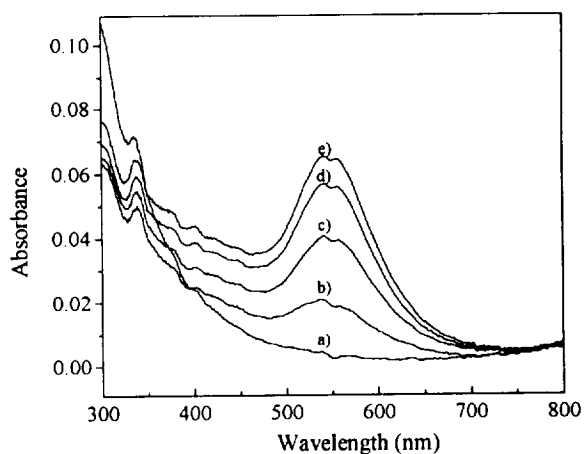


Figure 1. UV-visible absorption spectra of a 13 layer ODA LB film after exposure to UV light for: a) 0 min; b) 15 min; c) 20 min; d) 25 min; e) 30 min.

Transmission electron microscopy shows that arrays of particles ranging from 10-200 nm diameter are formed in the ODA and BDSAC films, and irregular arrays of larger particles are formed in the HDA films. AFM studies of ODA, HDA and BDSAC LB films not only confirm the results obtained by TEM in terms of size and shape of the gold crystals, but also reveal that the photoreduced metallic particles are rather thin. The surface analysis of a nine layer BDSAC LB film displayed in Figure 2 reveals a variation of the height of 15 ± 5 nm due to the presence of the gold nanoparticles. Similar values were obtained with ODA and HDA LB films. These results indicate that the gold crystals exhibit a high surface to volume ratio.

The observation of gold particles in some of the films and not others indicates that strong attractive electrostatic interactions exist between the positively charged polar heads of ODA, HDA and BDSAC and the AuCl_4^- anions present in the subphase. These electrostatic forces allow the transfer of the anionic species during the LB film deposition. As the zwitterionic polar heads of DPPS and DPPC do not induce similar attractive interactions, few gold anions are transferred onto solid substrates using these lipids as templates. Moreover, comparison of the films after particle growth indicates that, under our experimental conditions, the ODA monolayer binds the AuCl_4^- anions more efficiently than the BDSAC and HDA films because of a higher charge density.

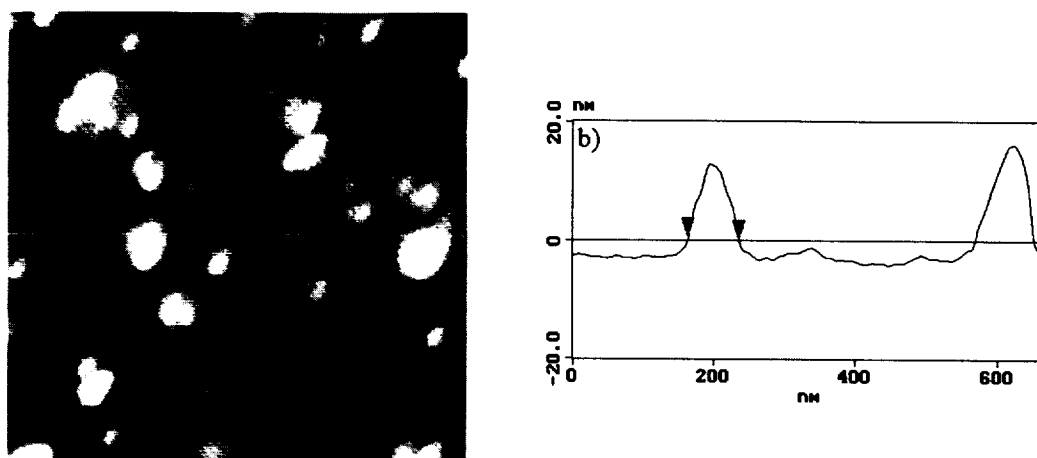


Figure 2 (left) AFM image (700x700 nm) and (right) corresponding section analysis of a 9 layer BDSAC LB film deposited onto a silicon wafer and exposed to UV light for 120 min.

Free Standing Bilayer Templates.

Templating in free standing bilayers can be used to produce metal platelets as well as the semiconductors previously described.¹¹⁻¹³ Figure 3 shows the effect of preparing silver and platinum particles in a bilayer system with little or no metal ion binding at the polar head group. In contrast the amine co-surfactant system (pentylamine/sodium dodecylsulfonate-toluene-water) and a bilayer composed of water and octylamine produces tabular-shaped Pt and Ag particles, respectively. A variety of metallic platelets have been prepared in the water-octylamine system including Au, Cu, and Ag/Pd alloys of special interest to the electronics community.

In addition to the templated synthesis of metal particles we have begun studies on two additional facets of self-assembled systems, enzyme catalyzed particle synthesis¹⁴ and room temperature synthesis of metal oxides.¹⁵ In the former work a urea-urease substrate-enzyme couple was used to synthesize aluminum basic sulfate from 15°C to 40°C by exploiting the pH increase created by the urease mediated breakdown of urea to ammonia and carbonate. Under certain conditions discrete, submicron, spherical $\text{Al}(\text{OH})_x(\text{SO}_4)_y$ particles were produced via precipitation from homogeneous solution in contrast to the large particles of broad size distribution produced by the more traditional thermal breakdown of urea. It was shown in extended kinetic studies at 25°C that the anhydrous metal oxide is the stable phase of both undoped and Y-doped zirconia, an important material for a variety of applications including structural ceramics and high temperature fuel cells. Experiments are anticipated that will combine the enzyme-induced precipitation reactions with low temperature synthesis within bilayer self-assembly systems to produce unique particles of heretofore thermodynamically intractable materials such as Y-doped zirconia and optoelectronic materials such as CuInSe_2 .

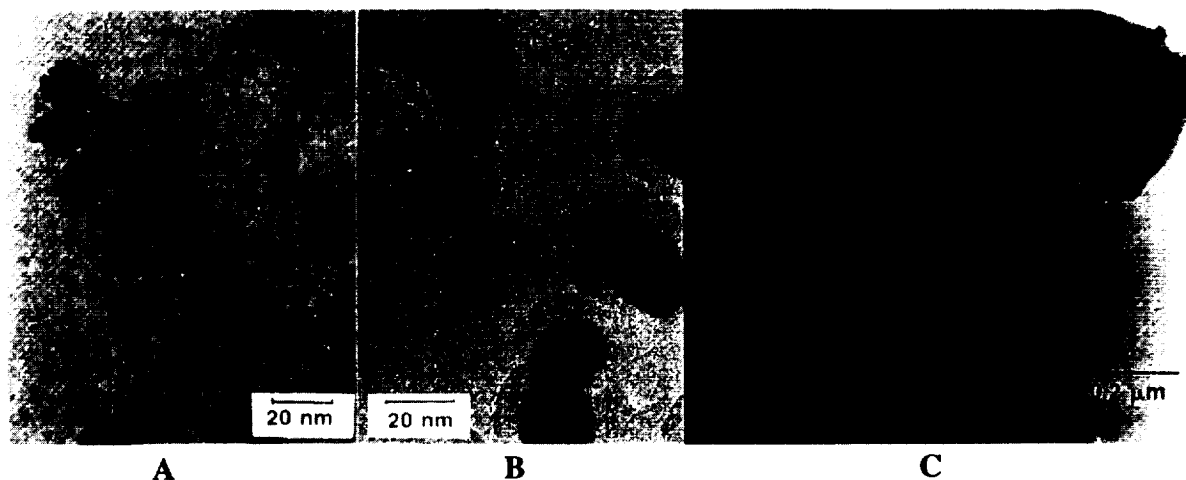


Figure 3. TEM photomicrographs of Pt and Ag particles produced in bilayer systems. (A) Pt particles produced in an AOT-heptane-water bilayer system without specific polar group templating; (B) Pt particles produced in a pentylamine/sodium dodecylsulfonate-toluene-water bilayer system with specific polar group templating and; (C) Ag particles produced in an octylamine-water bilayer with templating.

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